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Nanoscale femtosecond spectroscopy for material science and nanotechnology

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Abstract

The design and implementation of a novel facility to perform ultrafast spectroscopy and three-dimensional (3D) fabrication at the nanoscale is reported. Single and multiphoton femtosecond excitation coupled to a laser scanning confocal microscope and a photon counting streak camera system allows to perform photoluminescence (PL) spectroscopy with in-plane spatial resolution of the order of 100 nm and temporal resolution of ∼2 ps. The facility combines high performance imaging capabilities in 3D with high sensitivity detection system and time-resolution of the photoluminescence. Imaging and spectroscopy are performed on the same spatial position thus allowing a direct correlation of the morphological features with the spectroscopic properties. The use of a laser scanning confocal microscope gives the advantages of far-field microscopy (possible sample perturbation as in the case of near-field technique is prevented) with spatial resolution well below the diffraction limit, and fast laser scanning for fast data acquisition and lower sample photodegradation. A possible application of this optical nano-probe is in the spectroscopic investigation and imaging of the active areas of molecular electronic and optoelectronic devices, such as TFTs, LEDs and PVs cells. The morphology of active layers within working devices can be correlated to field distributions, charge flows, charge recombination and light emission. We show the potential of this novel experimental set-up for the study of organic, hybrid, biological nanostructures and nanodevices.

Keywords: Nanoscale ultrafast spectroscopy; Confocal microscopy; Two-photon excitation microscopy; Nanotechnology

1. Introduction

Confocal laser microscopy is experiencing intense development not only in the traditional area of cell biology, but also in other scientific and technological fields, such as material science and nanotechnology [1,2], where it can provide unprecedented probing and fabrication tools. With respect to near-field microscopy [3], which can reach lateral resolution down to few nanometers [4,5], far-field confocal microscopy [6] has a lower lateral resolution that approach 100 nm [7]. However, in particular in the laser scanning version, confocal microscopy and spectroscopy remains attractive for nanoscale investigations; as it is less invasive and perturbing (especially important for soft matter), can perform three-dimensional (3D) imaging [6] and fast data acquisition. The latter may become extremely important to prevent sample photodegradation.

In addition, confocal laser microscopy allows straightforward axial tomography even in the presence of opaque samples by using two- or three-photon absorption to enhance laser penetration within the sample [8,9].

Laser scanning confocal microscopy and spectroscopy can be a key tool for material science and nanotechnology, as it may probe fundamental electronic and optical properties at the relevant nanoscale. A direct correlation of the spectroscopic properties of materials and devices with morphological features can be achieved at the nanoscale, thus providing fundamental understanding of nanostructured materials and devices. In the case of organics, for example, evidences are available that tailoring the morphological characteristics of thin films directly affects the performance and working conditions of optoelectronic devices, such as OLEDs, OTFTs and OPVs cells [10,11]. In this view, there is urgent need of a detailed microscopic understanding of field distributions, charge flows, charge recombination and light emission in the active layers of devices.

In this paper, we report on a novel integrated facility for optical probing and 3D fabrication at the nanoscale, based on ultrafast and continuous laser excitation, confocal laser

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scanning microscope, continuous and time-resolved detection of photoluminescence (PL). The facility allows direct correlation between nano-architectures and spectroscopic response with in-plane spatial resolution of the order of 100 nm and temporal resolution of ∼2 ps.

Moreover, the system permits fabrication of three-dimensional nanostructures via spatially selected photobleaching of photosensitive materials or via two-photon initiated photo-polymerization [12]. 3D structures can be computer designed with a final resolution of the order of 200 nm [13].

2. Experimental set-up and application to organic nanostructured thin films

In Fig. 1 is reported the experimental set-up of the nanoscale femtosecond facility based on a confocal laser scanning microscope, a Ti:sapphire femtosecond/picosecond laser, three single line cw lasers (405, 488 and 543 nm), three parallel channels for integrated PL detection centered at selected spectral ranges in the visible and a streak camera for time-resolved PL measurements.

The optical microscope is a Nikon Eclipse TE-2000-E in the inverted configuration equipped with a single pinhole confocal scanning head. Fig. 2 shows a schematic of the confocal laser scanning head, whose main components are the confocal pinhole and the galvanometric scanning mirrors. The pinhole is optically conjugated to the focal plane of the microscope and cuts the sample luminescence from above and below the focal plane, thus increasing the overall spatial resolution [6].

The galvanometric mirrors provide precision scanning of the laser beam on the sample surface, while the axial tomography is obtained by scanning the sample through the focal plane with minimum step of 50 nm. The *xyz* spatial control of laser excitation allows the imaging of the sample by sequential detection of the photoluminescence intensity. In order to develop the scanning confocal microscope as a spectroscopic tool, several dichroic mirrors (Fig. 2) with complementary spectral properties that allow PL spectra measurements in the entire visible range were custom designed to be inserted in the scanning head. The three cw excitation lasers are coupled either independently or contemporarily into the microscope through a multimode optical fiber, thus permitting simultaneous excitation of different chromophores and electronic excited states. Sample imaging is achieved by detecting sample photoluminescence with three independent photomultipliers, each centered in a complementary spectral window of the visible range. The independent detection channels provide information on the spatial location of chromophores or electronic states emitting at different wavelengths.

The spatial resolution of the photoluminescence images depends on the confocal pinhole diameter, and is proportional to the ratio between the laser excitation wavelength and the objective numerical aperture (NA)

$$\text{resolution} \sim 0.37\left(\frac{\lambda^*}{\text{NA}}\right) \quad \text{with } \lambda^* = (\lambda_{\text{exc}}\lambda_{\text{emiss}})^{1/2} \tag{1}$$

$$\text{resolution} \sim 0.51\left(\frac{\lambda_{\text{exc}}}{\text{NA}}\right) \tag{2}$$

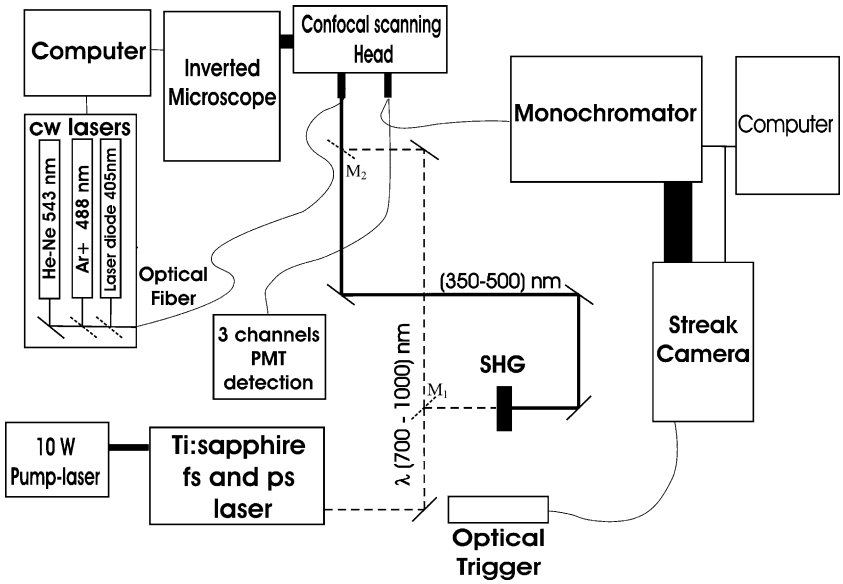

Fig. 1. Schematic of the nanoscale femtosecond facility for material science and nanotechnology. The system has femtosecond, picosecond and continuous laser excitation sources coupled to a confocal laser scanning microscope and to a detection set up for integrated and time-resolved photoluminescence measurements. 3D imaging of samples is performed by mapping of one- or two-photon excited photoluminescence with controlled laser scanning. Samples can be excited simultaneously by three independent laser lines and photoluminescence imaging at three selected wavelength ranges can be acquired simultaneously. Pulsed excitation switch from the range 700–1000 nm to the range 350–500 nm is achieved by insertion/removal of M1 and M2 mirrors.

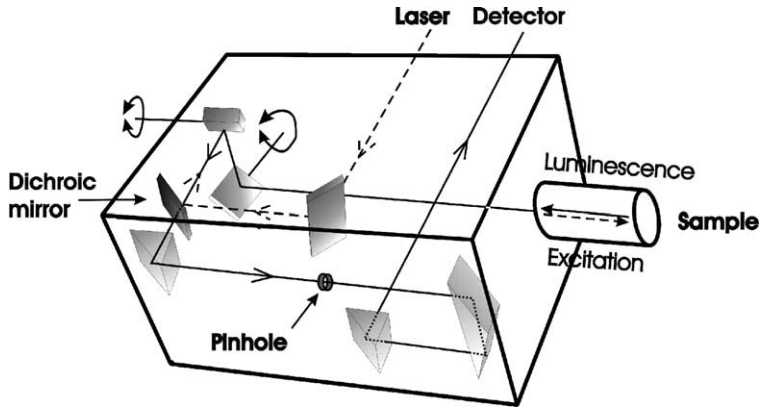

Fig. 2. Schematic of the single pinhole compact confocal scanning head. The incoming laser beam is reflected by the dichroic mirror and scanned onto the sample by two galvanometric mirrors. The sample photoluminescence is collected through the same optical path, being transmitted by the dichroic mirror. The pinhole selects the portion of the sample contributing to the photoluminescence which reaches the detectors.

Eq. (1) refers to the theoretical approximation for a pinhole aperture smaller than 0.25 Airy units (AU), where 1 AU = $(1.22\lambda_{exc})/NA$ while the second is valid for aperture ranging from 1 Airy unit to infinite aperture [6]. From Eq. (2) by using oil immersion objective with numerical aperture as high as 1.3 and excitation wavelength of 400 nm it is possible to obtain in-plane resolution of ∼160 nm and axial resolution (z) of ∼480 nm.

The facility is further provided with a mode-locked Ti:sapphire femtosecond/picosecond laser, pumped at 532 nm by a solid state 10 W cw laser. The Ti:sapphire laser has tunable emission in the range between 700 and 1000 nm, with pulse duration of ∼100 fs and repetition rate of 80 MHz. The pulsed laser is directly coupled into the scanning head with external optics. The set up design is such to minimize the pulsed laser beam path through transmission optics in order to minimize pulse broadening. The laser pulse duration is estimated to be of the order of few hundred femtosecond at the microscope focal plane.

The second harmonic of the Ti:sapphire laser is used to extend the excitation wavelength in the range 350–500 nm and is generated by coupling the Ti:sapphire laser beam into a β-barium borate (BBO) nonlinear crystal. Two easy to change optical paths (see Fig. 1) are used for the 350–500 nm and the 700–1000 nm pulsed excitation ranges. The Ti:sapphire fundamental laser emission provides excitation energy that can be used for two-photon excitation (TPE) in organics, while the doubled frequency laser beam is used for single photon excitation.

By two-photon excitation it is possible to achieve sample imaging and 3D structures nanofabrication with resolution of about 200 nm [13]. In this case, the spatial resolution is given by the sample volume where there is the probability for the material to absorb coherently two photons of the incoming laser beam. The two-photon absorption is proportional to the square of the electromagnetic field intensity, which confines the non-linear process in a small portion of the irradiated spot in the sample [14].

An Hamamatsu streak camera system with a temporal resolution of ∼2 ps coupled to a monochromator is used to spectrally resolve photoluminescence and to measure its time evolution. The output fiber of the confocal microscope is coupled to the streak camera allowing the association of time-resolved PL spectra to the selected spatial position on the sample. The set-up can additionally be used to map, with nanoscale resolution, the emission in light emitting devices as, e.g. OLEDs. Spatially controlled laser excitation can provide correlation between action spectra and local film morphology in photovoltaic devices.

As an illustrative example of the morphological–spectroscopic information which can be obtained with the presented facility, we consider thin films of conjugated materials which are relevant for molecular electronics and

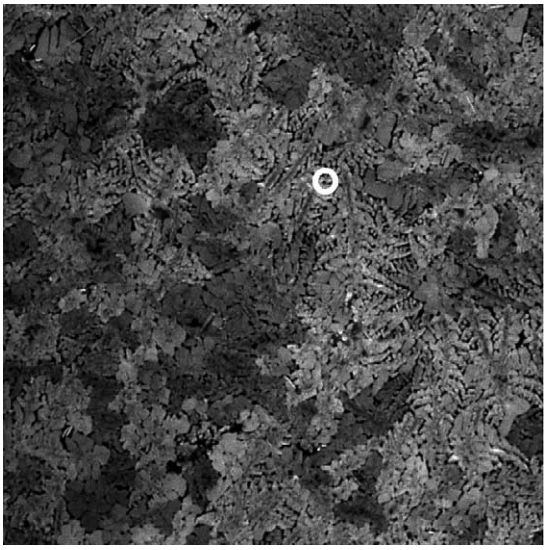

Fig. 3. Confocal photoluminescence image of a 50 nm thick film of tetracene grown by high vacuum sublimation. Sample photoluminescence has been excited by the second harmonic of the femtosecond Ti:sapphire laser at 400 nm. Lateral dimension of the confocal image is 100 μm.

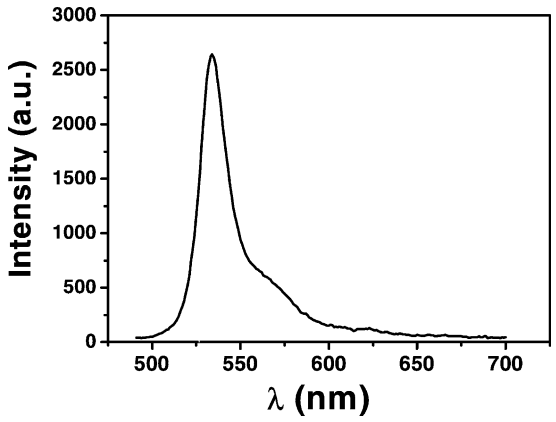

Fig. 4. Photoluminescence spectrum of the selected portion of the tetracene film indicated in Fig. 3 by the white circle. Photoluminescence excitation conditions are the same used to image the sample, i.e. second harmonic of the femtosecond Ti:sapphire laser at 400 nm.

optoelectronics. Fig. 3 shows a confocal PL image of a tetracene film with 50 nm thickness grown by high vacuum sublimation. The sample has been imaged with a 40 times magnification oil immersion objective and photoluminescence has been excited with the second harmonic of the Ti:sapphire laser at 400 nm. Detection of the spatially resolved PL intensity is performed with the PMT, whose sensitive spectral window is centered at 515 nm. Fig. 4 reports the PL spectrum of the tetracene film originated from the sample area circled in white in Fig. 3. The corresponding PL time decay at 525 nm is given in Fig. 5. By selecting the spatial position of the spectroscopic analysis we can directly correlate the morphological features to the photophysical properties in nanostructured samples.

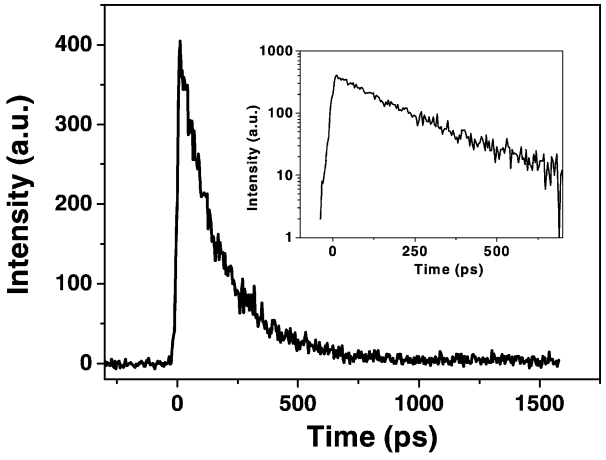

Fig. 5. Time-resolved photoluminescence decay at 525 nm of the portion of tetracene thin film indicated in Fig. 3 by the white circle. Photoluminescence excitation conditions are the same used to image the sample and to measure the steady state spectrum, i.e. second harmonic of the femtosecond Ti:sapphire laser at 400 nm. The inset shows the photoluminescence decay in logarithmic scale.

In conclusion, we reported the design and implementation of a novel experimental facility that allows to perform nanoscale 3D imaging, ultrafast spectroscopy, and photonic fabrication at the nanoscale. We discussed the great potential of this tool when applied to material science and nanotechnology. The presented set-up offers novel opportunities to investigate the photophysical properties of organic, hybrid and biological nanostructures and nanodevices.

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